# One-step synthesis of core(Cr)/shell(gamma-Fe2O3) nanoparticles

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*Published in:*
Journal of the American Chemical Society

*DOI:*
10.1021/ja0443225



*Publication date:*
2005

# 1 Characterization Techniques

## *1.1 Synchrotron Powder X-ray Diffraction*

Experiments were performed at the beamline X7A of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory with a linear position-sensitive detector gating electronically on the Kr-escape peak. Monochromatic x-rays were obtained using a water-cooled Ge111 channel cut monochromator. The instrumental resolution in this setup, $\Delta d/d$, is ~ $10^{-3}$. The sample was contained in an unsealed 0.3 mm capillary, which was rotated at a frequency of roughly 1 Hz to reduce preferred sample orientation effects.

## *1.2 Transmission Electron Microscopy (TEM)*

Nanocrystal size and morphology were investigated using a Phillips CM-12 Transmission Electron Microscope (100 KeV). Nanocrystals suspended in toluene, were deposited onto a carbon stabilized Formvar-coated copper grid (400 mesh) and allowed to dry.

### 1.2.1 Magnetic measurements

Magnetic data of the solid samples were collected with a Quantum Design SQUID MPMS-XL (AC and DC modes and maximum static field of ± 5 T) both in liquid helium and room temperatures. The temperature dependence of the magnetization was measured in the range 5 - 400K in an applied field of 20 Oe, after cooling in zero magnetic field (ZFC) or by cooling in a field of 20 Oe (FC).

### *1.3 Mössbauer Spectroscopy*

Mössbauer measurements were performed using a constant acceleration HALDER-type spectrometer with a room-temperature $^{57}Co$ source (Rh matrix) in transmission geometry. The polycrystalline absorbers containing about 10 mg $cm^{-2}$ of iron were used to avoid the experimental widening of the peaks. The spectra at 4.2 and 293 K were recorded using a variable-temperature cryostat. The velocity of the $^{57}Co$ source was calibrated using pure iron metal as the standard material. The refinement of the Mössbauer spectra showed an important and abnormal widening of the peaks, so that the spectra were fitted assuming a distribution either of quadrupolar splittings or of hyperfine fields.

### *1.4 HR-TEM and EELS Experimental*

Specimens were prepared by touching the dry powder with C/Collodion coated Cu grids. High-resolution transmission electron microscopy measurements were performed on a FEI Tecnai F-30 UT operating at 300kV and equipped with a field emission gun. Energy filtered imaging and electron energy loss spectroscopy (EELS) were performed using Gatan Image Filter (GIF).

## 2 Magnetic Measurement Results

The magnetic properties of the core/shell nanoparticles were studied by using SQUID at field range of ± 5 T (H-M) and the temperature range from 2 to 300 K (T-M). H-M measurements from SQUID were used to observe the induced magnetization from the materials in the applied field. Figure 1 illustrates the H-M data. The measurements

show no coercivity at room temperature. A hysteresis appears with 1500 Oe, as the coercivity at 5 K. This is the typical H-M behavior for superparamagnetic materials. The magnetization at 5 T is ~ 23 emu/g for measurements at 295 K and 32 emu/g for measurement at 5 K, after the polymer content (60% weight loss by TGA) has been

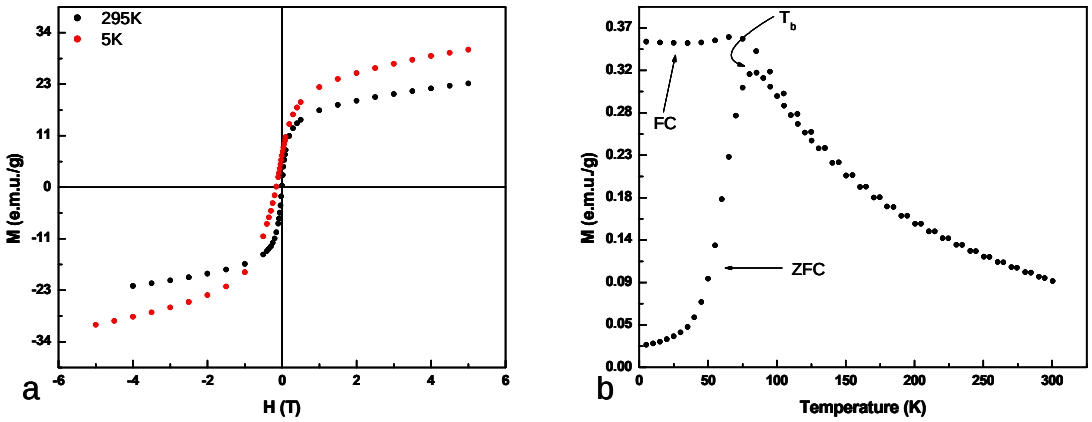



**Figure 1. (a) H-M measurements; (b) T-M measurements.**

subtracted.

The saturation moment is 76 emu/g for γ-$Fe_2O_3$ and 210 emu/g for Fe, and Cr is paramagnetic material. The particles size is a possible explanation why the magnetic moment of the sample particles is significantly lower than the literature values. When particles are small, their magnetic order is easier to be randomized, so it is hard to reach the saturation moment. Since the magnetic moment of Fe is much higher than that of γ-$Fe_2O_3$, this should enhance the overall magnetic moment. However, this is not observed here. This is another evidence suggesting that the metal component in the particle should be Cr and not Fe. From the T-M measurements (Figure 1), the maximum of the ZFC curve shows that $T_b$ is 85 K. The fact that the ZFC and the FC curve overlap above $T_b$ is an indication of a narrow particle size distribution. Overall, the materials behave as typical superparamagnetic materials.

# 3 Synchrotron Powder X-Ray Diffraction

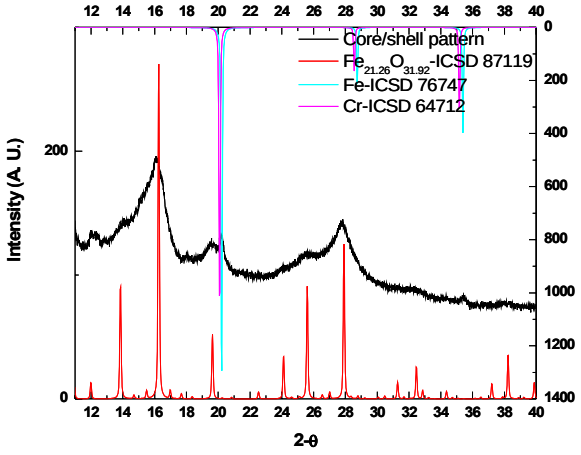



**Figure 2. Synchrotron powder XRD pattern of the sample.**

# 4 Mössbauer Spectroscopy Results

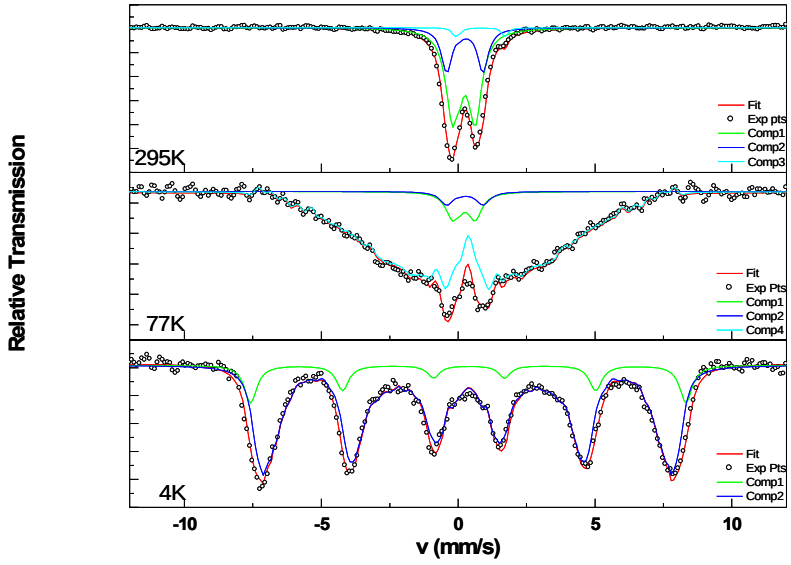



**Figure 3. Mössbauer spectrum.**

# 5 Materials Balance Calculation

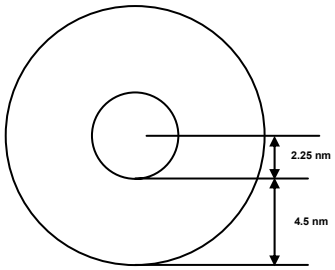
The molecular weight, *M.W.*, of Cr and Fe are

$M.W._{Cr} = 52.0$ and $M.W._{Fe} = 55.8$.

The density, $\rho$, of $Fe_2O_3$, $Fe_3O_4$ and Cr are

$\rho_{Fe_2O_3} = 5.24\,{}^{g}\!/_{cm^3}$, $\rho_{Fe_3O_4} = 5.10\,{}^{g}\!/_{cm^3}$, and $\rho_{Cr} = 7.19\,{}^{g}\!/_{cm^3}$.

The radius, *r*, of particle, core, and shell are




$r_{particle} = 6.75nm$, $r_{core} = 2.25nm$, and $r_{shell} = 4.5nm$.

The volume, *V*, of particle, core and shell are

$V_{partricle} = \frac{4}{3}\pi r_{particle}^3 \approx 1288nm^3$, $V_{core} = \frac{4}{3}\pi r_{core}^3 \approx 47nm^3$, and

$V_{shell} = V_{particle} - V_{core} = 1241nm^3$.

The results of Mössbauer spectra are

$Fe^{3+}$ = 96.57% and $Fe^{2+}$ = 3.43%.

EELS

| Region | Element Cr | Fe |
|---|---|---|
| Particle | 1.1 | 9.3 |
| Shell | 0.3 | 6.3 |

This is atomic ratio and needs to be converted to weight basis, so the result is as follows

| Region \ Element | Cr | Fe |
|---|---|---|
| Particle | 57.2 | 518.94 |
| Shell | 15.6 | 351.54 |

Assumption: Cr only exists as metal form.

Based on Mössbauer spectra, there is small amount of $Fe^{2+}$, which is the result of $Fe_3O_4$. From this we can calculate the portion of $Fe_3O_4$ and $Fe_2O_3$. In the from of $Fe_3O_4$, $Fe^{2+}$:$Fe^{3+}$ = 1:2. It takes two $Fe^{3+}$ to have $Fe_2O_3$. Therefore, the ratio $Fe_3O_4$:$Fe_2O_3$ is $3.43 : {}^{96.57-2\times3.43}\!/_{2}$. The density of the particle, $\rho_{particle}$, is

$$\rho_{particle} = \frac{57.2}{57.2+518.94}\rho_{Cr} + \frac{518.94}{57.2+518.94}\frac{3.43}{3.43+{}^{96.57-2\times3.43}\!/_{2}}\rho_{Fe_3O_4} + \frac{518.94}{57.2+518.94}\frac{{}^{96.57-2\times3.43}\!/_{2}}{3.43+{}^{96.57-2\times3.43}\!/_{2}}\rho_{Fe_2O_3} = 5.42\,{}^{g}\!/_{cm^3},$$

so the weight of the particle, $W_{particle}$, is

$$W_{particle} = \rho_{particle} \times V_{particle} = 6987\times10^{-28}\,g.$$

The density of shell, $\rho_{shell}$, is

$$\rho_{shell} = \frac{15.6}{15.6+351.54}\rho_{Cr} + \frac{351.54}{15.6+351.54}\frac{3.43}{3.43+{}^{96.57-2\times3.43}\!/_{2}}\rho_{Fe_3O_4} + \frac{351.54}{15.6+351.54}\frac{{}^{96.57-2\times3.43}\!/_{2}}{3.43+{}^{96.57-2\times3.43}\!/_{2}}\rho_{Fe_2O_3} = 5.31\,{}^{g}\!/_{cm^3},$$

so the weight of the shell, $W_{shell}$, is

$$W_{shell} = \rho_{shell} \times V_{shell} = 6594\times10^{-28}\,g.$$

From the above result we can calculate the weight of core, $W_{core}$, and its density, $\rho_{core}$.

$$W_{core} = W_{particle} - W_{shell} = 393\times10^{-28}\,g,$$

so $\rho_{core} = \dfrac{W_{core}}{V_{core}} = 8.36\,{}^{g}\!/_{cm^3} > \rho_{Cr}$.

# 6 Reaction mechanism of core(Cr)/shell(γ-$Fe_2O_3$) nanoparticles.

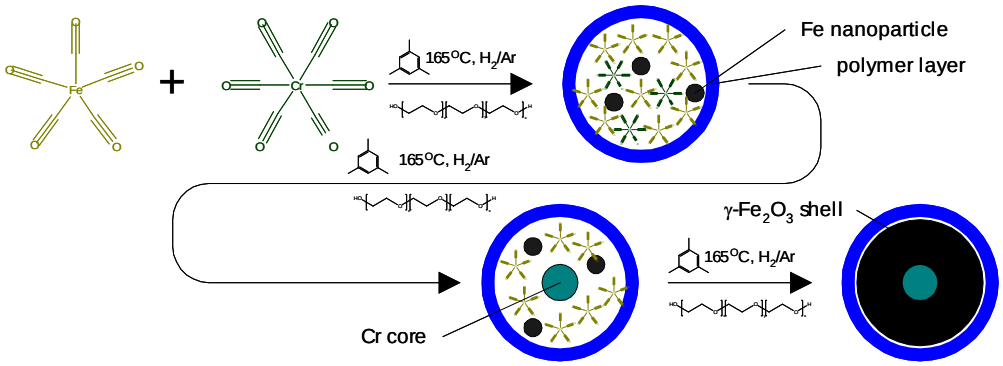



**Figure 4. Synchrotron powder XRD pattern of the sample.**